



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Principle of Photocatalysis Reaction

The word “photocatalysis” comes from photochemistry and catalysis. So, the photocatalytic process implies that light and a catalyst are used together to accelerate chemical transformations. The difference between conventional catalysis and photocatalysis is the mode of activation of the catalyst, in which the thermal activation is replaced by a photonic activation (Herrmann, 1999).

The photocatalytic process involves the utilization of a semiconductor. Most semiconductors are the oxide or sulfide of metals. When semiconductors are illuminated with light at an appropriate wavelength, they generate powerful oxidants, which will convert most organic materials into carbon dioxide, water and inorganic compounds. This process is effective in destroying a wide range of organic materials (Robertson, 1996). The organic compounds containing phosphorus, sulfur and halogen heteroatoms may be oxidized quantitatively yielding phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and halide (X^-), respectively (Choi and Hoffmann, 1995).

The basic principle of photocatalysis can be described as follows. A semiconductor (SC) is characterized by an electronic band structure that are occupied valence band (νb) and unoccupied conductance band (cb). These two bands are separated by the energy gap called the “band gap” (E_{bg}). When the semiconductor is illuminated with light that has energy higher or equal to the band gap, and electron from the νb is promoted to the cb with the simultaneous generation of a hole (h^+) in the νb as illustrated in Figure 2.1.

Possible reactions that can occur when a solution containing a semiconductor absorbs a photon ($h\nu$) of a suitable wavelength are shown in the following reactions (Robertson, 1996).



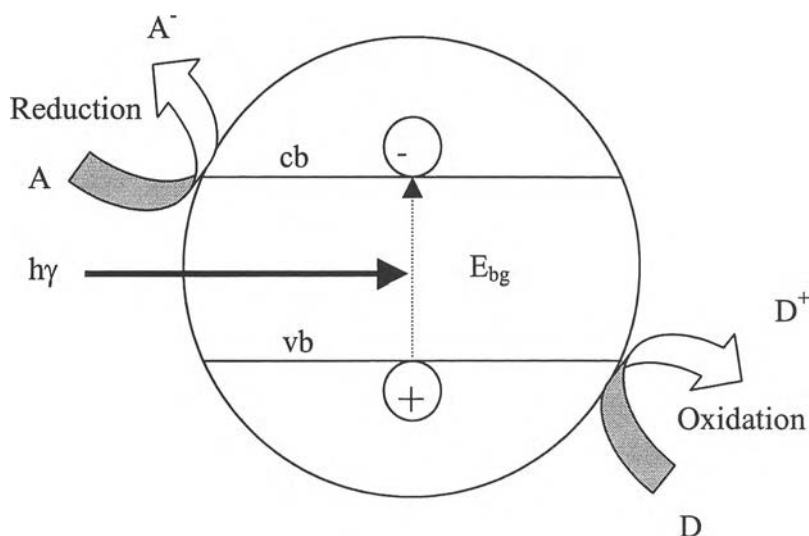


Figure 2.1 Promotion of an electron from the valence band to the conduction band on illumination of a semiconductor (Litter, 1999).



The electron and hole pair may recombine on the surface or in the bulk of the particles in a few nanoseconds with the generation of heat or can be trapped in surface state where they can react with other species that are adsorbed or close to the surface of particles. For example, if an electron donor or species D is adsorbed on the surface, it will react with the hole and the oxidation reaction occurs. On the other hand, if an electron acceptor or species A is adsorbed on the surface, it will receive an electron and the reduction reaction occurs. The energy level at the bottom of the cb is the reduction potential of photoelectron and the energy level at the top of the vb determines the oxidizing ability of photohole. From thermodynamic points of view, adsorbed species can be reduced photocatalytically by the cb electrons if they have redox potentials more positive than the flat band of the cb and can be oxidized by the vb holes if they have redox potentials more negative than the flat band of the vb (Litter, 1999).

In the photocatalytic oxidation of organic molecules, there are two possible mechanisms when a semiconductor is illuminated with photon energy greater or

equal to its band gap energy. Those are direct hole oxidation and OH^\bullet oxidation (Ilisz and Dombi, 1999). Normally, OH^\bullet oxidation tends to be the main mechanism in the photocatalytic oxidation. For the direct hole oxidation, the photohole reacts directly with the adsorbed organic molecules as shown in equation (2.3) while, for the OH^\bullet oxidation, the photohole reacts with surface hydroxyl group (OH^-) or adsorbed water and hydroxyl radical (OH^\bullet) will be formed. This hydroxyl radical has a high oxidation potential. It can react rapidly and non-selectively with most organic compounds and convert them into carbon dioxide, water and other inorganic compounds (De Lasa *et al.*, 1992). The OH^\bullet oxidation reactions are the followings:



The recombination must be avoided because it inhibits the oxidation reaction. Adding some electron scavengers such as oxygen molecules will delay the recombination since they can trap electrons out from the positive hole and transform into superoxide radical ion ($\text{O}_2^{\bullet-}$) and leading to the additional formation of hydroxyl radical (Litter, 1999).



As reported by De Lasa *et al.* (1992), both H_2O and O_2 are essential species in the photocatalytic process. Photocatalytic oxidation of 4-CP does not occur in the absence of either H_2O or O_2 .

2.2 Types of Semiconductors

A semiconductor used as photocatalyst should be an oxide or sulfide of metals such as TiO_2 , CdS and ZnO . The energy band gap of the photocatalyst should

match the energy gained from a light source. The valence band, conductance band, band gap and band gap wavelength of some common semiconductors are shown in Table 2.1.

TiO₂ is a popular photocatalyst because the band gap is considerably high around 3.0 eV. It can be activated in the near ultraviolet light (~ 380 nm). Other types of semiconductors that can be used as photocatalysts such as ZnO or CdS may not be applicable due to their toxicity. Moreover, ZnO is corroded by illumination in aqueous solution and toxic Zn²⁺ is found (De Lasa *et al.*, 1992). CdS also has the toxicity problem due to CdS photocorrosion (Reutergardh and Iangphasuk, 1997). TiO₂ is more stable and insoluble in aqueous solution than ZnO and CdS. It has been shown that TiO₂ does not lose its activity when reused (De Lasa *et al.*, 1992). Apart from its highly corrosive resistance, TiO₂ is considerably inexpensive. Therefore, TiO₂ is suitable for the photocatalytic process. Generally, there are three different forms of TiO₂ namely anatase, brookite and rutile. TiO₂ in the anatase form has been observed to be active and stable over very long irradiation times (Cheng *et al.*, 1995).

Table 2.1 The band positions of some common semiconductor photocatalysts (Robertson, 1996)

Semiconductor	Valence band (eV)	Conductance band (eV)	Band gap (eV)	Band gap wavelength (nm)
TiO ₂	+3.1	+0.1	3.0	380
SnO ₂	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO ₃	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887

2.3 Metal-Loaded TiO₂

Brezova *et al.* (1997) studied the phenol decomposition using different metal-loaded TiO₂ photocatalysts prepared on glass fibers by the sol-gel method. The metals used in this study were Li⁺, Zn²⁺, Cd²⁺, Ce³⁺, Cr³⁺, Co³⁺, Fe³⁺, Al³⁺, Mn²⁺ and Pt⁰ and all metals were loaded at 5 mol% metal/TiO₂. The presence of metals such as Li⁺, Zn²⁺, Cd²⁺ and Pt⁰ improved the photoactivity of the TiO₂ layer prepared on glass fibers by the sol-gel technique. On the other hand, the presence of Ce³⁺, Cr³⁺, Co³⁺, Fe³⁺, Al³⁺ and Mn²⁺ in the TiO₂ layer supported on glass fibers has a detrimental effect on the photoactivity of phenol decomposition. The deleterious effect was explained by the fact that trivalent and pentavalent ions behave as recombination centers of the photoproduced charge carriers.

Blazkova *et al.* (1998) studied the photocatalytic decomposition of phenol on sol-gel immobilized TiO₂ with varying %Pt loading. The Pt loading was varied from 0.5-5.0 mol% Pt⁰:Ti⁴⁺. The best result was obtained for Pt/TiO₂ with 1.25 mol% Pt. For the concentration of Pt ≥ 5 mol%, it was found to have a pernicious effect on the photocatalyst activity. The major role of Pt on TiO₂ is to accelerate the superoxide radical anion O₂^{•-} formation and consequently decrease the recombination. The increasing of Pt loading to a certain level causes the electron transfer of photoelectron from the semiconductor to the metal particles, decrease of O₂^{•-}, resulting in the increase of recombination and decrease of the photocatalytic activity for phenol decomposition.

Phuaphromyod (1999) studied the photocatalytic degradation of isopropyl alcohol using Pt, TiO₂, and Pt/TiO₂. Pt or TiO₂ alone showed a low activity but Pt/TiO₂ had a much higher activity for the degradation of isopropyl alcohol.

Tharathonpisutthikul (2000) studied the photocatalytic degradation of 4-CP by using TiO₂, Pt/TiO₂, TiO₂-SiO₂ and Pt/TiO₂-SiO₂ prepared by the sol-gel method. It was found that addition of a small amount of Pt into TiO₂ improved the catalyst activity and the highest activity was obtained with 1% Pt/TiO₂. For TiO₂-SiO₂ catalyst, the highest activity was achieved at 10% SiO₂-TiO₂ because of its highest adsorption capacity. For Pt/TiO₂-SiO₂ with 1% Pt and 10% SiO₂, although 1% Pt or

10% SiO₂ alone in TiO₂ could improve the catalytic activity, the synergistic effect of adding both 1% Pt and 10% Si was not observed due to the agglomeration of the catalyst, which, in turn, lowered the catalytic activity.

Moonsiri (2002) studied the effect of Ag/sol-gel TiO₂ on the degradation of 4-CP. A series of Ag/sol-gel TiO₂ were prepared at different Ag loadings from 0.2-1.5 mol%. 0.5 mM 4-CP and 0.5 g/l catalyst were used. It was found that the presence of Ag did not significantly affect the degradation of 4-CP but had the effect on the intermediate products and TOC degradation and 0.5 mol% Ag/sol-gel TiO₂ had a minimum value of TOC at 360 min. With a Ag content greater than 0.5 mol%, the TOC removal increased with increasing Ag loading. It was suggested that a small amount of Ag on TiO₂ attributes to the acceleration of superoxide radical anion, O₂^{•-}, formation resulting in decreasing the recombination process while enhances the photoactivity.

Mikula *et al.* (1995) studied the activities of sol-gel TiO₂ immobilized, Degussa P25 immobilized on glass fiber fabric and Degussa P25 suspension for the photocatalytic degradation of phenol. The result showed that the decreasing rate of phenol by using Degussa P25 suspension was higher than those with the immobilized systems.

2.4 Parameters Influencing the Photocatalytic Rate of Organic Degradation

2.4.1 Light Source

Stafford *et al.* (1997) investigated the effect of light wavelength on the rate of photocatalytic degradation of 4-CP. In this experiment, two lamps, a 450 W medium pressure mercury lamp ($\lambda > 340$ nm) and an 8 W black light lamp ($\lambda_{\text{max}} = 350$ nm), were used. Other parameters were kept constant. With the 8 W black light lamp, the rates were slower and the maximum concentration of intermediates was lower because of the lower light intensity. It was reported that when a lamp with lower intensity was used, subsequent reactions of intermediates occurred at relatively faster rates than that of the degradation of 4-CP. Therefore, the rate of mineralization was more rapid. This enhancement rate of mineralization at the lower

light intensity may occur because the slower rate of hole production allows the other species in solution to come into adsorption equilibrium with TiO_2 . The other reason is that when the lower wavelength is used, electrons adsorb more energetic photons and the higher energy electrons are less likely to recombine. Therefore, the photoactivity increases with decreasing light wavelength.

Blazkova *et al.* (1998) studied the effect of light sources on the phenol degradation using Pt/ TiO_2 immobilized on glass fibers. Four standard emission lamps were used as the irradiation sources, maximum intensity at 320, 350, 410 nm and white lamp resembling the solar spectrum. The highest photoactivity was obtained for the source with maximum intensity at 320 nm. This experimental result was consistent with the result published by Stafford *et al.* (1997). The photocatalytic activity significantly increased with decreasing wavelength. Although the white lamp resembling the solar spectra had lower efficiency, it showed that the prepared Pt/ TiO_2 catalysts may be used for solar applications.

2.4.2 Initial Concentration

The results from several works showed different trends of the effect of initial concentration on organic degradation. Some of the studies showed that the rate of organic degradation increased with increasing initial concentration. Surprisingly, some studies reported that the rate of degradation decreased with increasing initial concentration. Moreover, some reactions showed that the initial concentration had no significant effect on the process. Freudenhammer *et al.* (1997) found that the rate of dichloroacetic acid on fixed TiO_2 was lower with a higher initial concentration of reaction substrate while Theurich *et al.* (1996) showed the rate of 4-CP degradation increased with increasing initial concentration of 4-CP. Besides, Reutergardh *et al.* (1997) found that as the reactive black 5 (RB5) concentration increased, the quantities of intermediates increased as well. For competing through side reactions with the parent dye decomposition, an increase in dye concentration affected the light penetration into the solution. Therefore, at high initial dye concentrations, the optical density in the solution was lower and fewer photons reached the catalyst's surface.

Theurich *et al.* (1996) studied the photocatalytic degradation of 4-CP in Degussa P25 suspensions. The concentration of 4-CP was varied from 0.2 to 10 mM. The degradation rate was found to be a function of the initial 4-CP concentration, at least in a certain range, when the other parameters were kept constant. The degradation rate increased with 4-CP concentration and remained constant at 4-CP concentrations greater than 5 mM. One possible explanation for this behavior was given that the adsorption of the substrate molecule was rate limiting. This adsorption was described by the Langmuir-Hinsherwood (L-H) equation,

$$\frac{-d [4\text{-CP}]}{dt} = \frac{kK[4\text{-CP}]}{1+K[4\text{-CP}]} \quad (2.11)$$

where $d[4\text{-CP}]/dt$ is the rate of 4-CP degradation, k is the reaction rate constant, K is the adsorption coefficient of 4-CP and $[4\text{-CP}]$ is the concentration of 4-CP. For a high concentration of the pollutant, where saturation coverage of the TiO_2 surface is achieved ($K [4\text{-CP}] \gg 1$), the L-H equation simplifies to a zero-order rate equation.

$$\frac{-d [4\text{-CP}]}{dt} = k \quad (2.12)$$

For a very low concentration of 4-chlorophenol ($K [4\text{-CP}] \ll 1$), the L-H equation changes into a pseudo first-order kinetic law.

$$\frac{-d [4\text{-CP}]}{dt} = k'[4\text{-CP}] \quad (2.13)$$

with $k' = kK$ being the pseudo first order rate constant. Therefore, at a high initial concentration, the 4-CP degradation obeys the zero order kinetics while the degradation kinetics at the low concentration can be interpreted as an example of the first order kinetics.

2.4.3 Dissolved Oxygen

The presence of oxygen in the photocatalytic systems can significantly affect the fate of the photogenerated species, i.e., it reacts with the conduction band electrons to form superoxide anion radicals, and it combines with organic radicals generated by the hydroxyl radicals attack or by the reaction with photoholes.

Blazkova *et al.* (1998) observed the effect of oxygen flow on the degradation of phenol using Pt/TiO₂ immobilized on glass fibers. It was found that the phenol half-life decreased linearly with increasing the oxygen flow in the photocatalytic degradation of phenol. However, the oxygen flow higher than 5 dm³/min under the given conditions damaged the photocatalyst quality.

Phuaphromyod (1999) studied the effect of dissolved oxygen on the photocatalytic degradation of isopropanol. The experiments were carried out by flowing nitrogen, air and oxygen into the isopropanol solution to obtain different levels of dissolved oxygen of 0, 8.8 and 37.7 mg/l, respectively. For the saturated dissolved oxygen of 37.7 mg/l, isopropanol was degraded rapidly and completely within 1.5 hours. The same results were observed with 8.8 mg/l of dissolved oxygen. When nitrogen was bubbled into the solution to obtain zero dissolved oxygen, the results showed a slight decrease in the isopropanol concentration. It was suggested that the dissolved oxygen had an important role in the photocatalytic degradation of isopropanol since the oxygen molecule can act as an electron trap. The trap separated electrons from the hole and the recombination process was reduced. Hence, the photocatalytic activity increases with increasing the dissolved oxygen. In addition, the oxygen flow served as the stirring medium to enhance the mass transfer rates in the irradiated system.

Moonsiri (2002) studied the effect of dissolved oxygen on the 4-CP degradation with 0.5 g/l sol-gel TiO₂. The solution was aerated with nitrogen while the other experiment was carried out at a very high dissolved oxygen level. It was found that in the presence of oxygen, the degradation rates of 4-CP and TOC were much higher than those of the system without dissolved oxygen. The three intermediate products, hydroquinone, benzoquinone and hydroxyhydroquinone, were generated during the 4-CP degradation without dissolved oxygen but benzoquinone

was not generated during the 4-CP degradation in the presence of dissolved oxygen. It can be concluded that the dissolved oxygen not only reduces the intermediate concentrations but also reduces the type of the intermediate products.

2.5 Sol-Gel Method

TiO₂ can be synthesized by several different methods: (1) inert gas condensation, (2) flame synthesis by TiCl₄ oxidation, (3) oxidation-hydrothermal synthesis of metallic Ti, and (4) hydrolysis precipitation of titanium alkoxides or chlorides (Wang and Ying, 1999). The sol-gel process provides excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures (Ertl *et al.*, 1987). Besides, it is capable of producing photocatalysts with a high surface area. It involves the formation of a metal-oxo-polymer network from molecular precursors such as metal alkoxides or metal salts. The sol-gel process consists of the hydrolysis of metal alkoxides and subsequent polycondensation as follows:



where M = Si, Ti, Zr, Al, and R = alkyl group. The relative rates of hydrolysis and polycondensation strongly influence the structure and properties of the resulting metal oxides. Typically, sol-gel-derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and grain growth and may induce phase transformation (Wang and Ying, 1999).

Factors affecting the sol-gel process include the reactivity of metal alkoxides, pH of the reaction medium, water to alkoxide ratio, reaction temperature, and nature of solvent and additive. The water to alkoxide ratio governs the sol-gel chemistry and the structural characteristics of the hydrolyzed gel. High water to

alkoxide ratios in the reaction medium ensure a more complete hydrolysis of alkoxides, favoring nucleation versus particle growth. In addition, an increase in water to alkoxide ratio leads to reduce the crystallite size in the calcined catalyst. An alternative approach to control the sol-gel reaction rates involves the use of acid or base catalysts. It was reported that for a system with a water to alkoxide ratio of 165, the addition of HCl resulted in the reduction of the crystallite size from 20 to 14 nm for materials calcined at 450 °C. Besides, a finer grain size and a narrower pore size distribution with a smaller average pore diameter were also attained for the sample synthesized with HCl (Wang and Ying, 1999). The size of alkoxy groups in alkoxides also plays an important role in controlling the particle size. The titanium alkoxide contains bulky alkoxy groups such as titanium amiloxide reduces the hydrolysis rate, which is advantageous for the preparation of fine colloidal particles (Murakami *et al.*, 1999).